PCT
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

7922

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification [6] :
A23F 3/16, 3/40

A1

(11) International Publication Number: WO 99/21432

(43) International Publication Date: 6 May 1999 (06.05.99)

(21) International Application Number: PCT/EP98/06637

(22) International Filing Date: 9 October 1998 (09.10.98)

(30) Priority Data:
08/958,959 28 October 1997 (28.10.97) US

(71) Applicant *(for AU BB CA CY GB GD GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW only)*: UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).

(71) Applicant *(for all designated States except AU BB CA CY GB GD GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW)*: UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(72) Inventors: CIRIGLIANO, Michael, Charles; Lipton, Division of Conopco, Inc., 800 Sylvan Avenue, Englewood Cliffs, NJ 07632 (US). FARRELL, Francis, John; Lipton, Division of Conopco, Inc., 800 Sylvan Avenue, Englewood Cliffs, NJ 07632 (US). MCKENNA, Raymond, Thomas; Lipton, Division of Conopco, Inc., 800 Sylvan Avenue, Englewood Cliffs, NJ 07632 (US). ROTHENBERG, Paul, John; Lipton, Division of Conopco, Inc., 800 Sylvan Avenue, Englewood Cliffs, NJ 07632 (US).

(74) Agent: BUTLER, David, John; Unilever plc, Patent Dept., Colworth House, Sharnbrook, Bedford, MK44 1LQ (GB).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: FLAVOURING MATERIALS FOR USE IN TEA CONTAINING BEVERAGES

(57) Abstract

An aqueous based tea solids containing beverage is disclosed which also contains a sufficient amount of a selected substituted phehyl flavouring antimicrobial compound to prevent microbial outgrowth while simultaneously contributing to the pleasant flavour or the beverage thus making the beverage acceptable both organoleptically and microbiologically. Optionally selected "hurdles" or stepwise antimicrobial controls are also employed.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

FLAVOURING MATERIALS FOR USE IN TEA CONTAINING BEVERAGES

The present invention relates to the use of natural and synthetically prepared flagrant materials which also act as antimicrobials in aqueous based beverages containing tea solids. These materials are selected substituted phenyl compounds.

Background and prior art

Acidified and native pH ready-to-drink (RTD) tea beverages, in the 2.5-6.5 pH range regardless of packaging are known to be susceptible to spoilage. As compared to cans, tea beverages packaged in glass and plastic bottles (because of increased 02 ingress), as well as tea beverages at the higher range of the pH spectrum, are even more sensitive to yeast and mould spoilage than canned teas.

There are many different processes for preparing and packaging or bottling ready-to-drink (RTD) teas. For example, in one process the bottles can all be sterilised and the tea beverage first pasteurised and then bottled at high temperature. Each of these high temperature treatments requires a large capital investment for equipment and if there were many different bottling plants the costs of equipping each of these multiple plants with such high temperature equipment would be prohibitive if not impossible to justify.

Further all of these high temperature expedients are relatively inefficient and require a very high use of energy and excessive costs in addition to the original equipment costs. It is thus seen to be desirable to be able to prepare and bottle RTD teas without using such cost ineffective, energy intensive methods which also require a large initial investment in equipment.

This is particularly significant if bottling is scheduled to take place in a large number of pre-existing bottling plants.

In an effort to overcome these problems a stepwise approach was taken. The principal requirement was to produce an excellent flavoured tea beverage which is microbiologically acceptable and which can be shipped and stored in a normal distribution chain through various warehouses and retail consumer outlets. These requirements must be met while keeping costs to a reasonable level and using pre-existing bottling plants. This in turn necessitates minimising capital investment in specialised equipment such as high temperature sterilising and pasteurising equipment and water treatment equipment such as reverse osmosis (RO) equipment.

Studies revealed that all of the above conditions could be satisfied by initiating a series of "hurdles" or steps each of which was designed to use existing equipment and resources. This could be accomplished within a reasonable cost while improving the microbiological stability of the tea beverage without deleteriously affecting its delicate flavour.

The steps include employing water having a very low water hardness; using a pH of about 2.5 to 4.0; using selected sequestrants with the pH and water adjustments; using selected polyphospates in combination with the pH water and sequestrants; and using selected well known preservatives such as nisin, natamycin, sorbic acid and sorbates and benzoic acid and benzoates together with the low water hardness, the pH adjustment, sequestrants and polyphosphates. Together these steps contribute to the antimicrobial effect and thus individually each is incrementally antimicrobially effective.

Each of these steps produces at least incremental and frequently synergistic antimicrobial effects. None of them however contribute positively to the overall delicate flavour of the tea beverage, rather all of the steps taken are done to improve microbiological stability without negatively affecting the flavour. Thus, the incrementally antimicrobially effective amount must take into account the flavour profile of the tea.

Many preservatives are readily available for many diverse uses. However natural compounds which are primarily flavorants are not usually considered for their antimicrobial activity.

There have been some attempts to use selected natural materials as preservatives. One of them is illustrated in Japanese Patent application 571194,775 where cinnamic acid is used in combination with selected other organic acids including citric acid and sorbic acid.

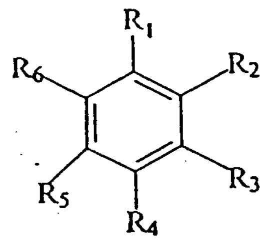
United States patent 5,431,940 takes the approach of stabilising beverages by using water having a low degree of hardness in combination with other preservatives and polyphosphates. The alkalinity is specified.

Tea containing beverages, because of their delicate balance of flavours require the utmost care in selecting preservatives. A fine balance must be achieved in stabilising teas without deleteriously affecting their flavour. Thus it is desirable to employ a natural compound as a flavourant which also may serve as an antimicrobial.

A method and composition is disclosed for imparting a pleasant flavour to tea beverages while simultaneously contributing to the control of microbial growth in ready-to-drink still and carbonated tea beverages, for distribution and sale at ambient or chilled temperatures. In addition a method and composition incorporating a stepwise or "hurdle" approach described above is disclosed. The beverages include herbal teas, both "still" and carbonated as well as black, oolong and green tea. The method uses selected compounds in optional combination with the hurdle or step approach. These natural compounds may be obtained naturally or synthesised.

The method, which also contributes to the stability of tea beverages employs a class of chemical compounds characterised by a structure containing an aromatic base, preferably an aromatic acid such as phenylbutenoic or phenylhexenoic acid and selected derivatives.

Generally the aromatic based compounds are as follows:



wherein R_1 is an unsaturated, non-halogenated side chain having up to about 9 carbons, one of which is preferably a carboxyl group, which may or may not be esterified, and the side chain has at least one double bond. The R_1 side chain preferably has up to about 6 carbon atoms. The R_1 side chain may contain unsaturated molecular components from the ester, alcohol, ketone or acid families. The compounds contain, as well, additional R_{2-6} groups occupying the other sites on the benzene ring where R_{2-6} may be the same or different and may be hydrogen or a low molecular weight non-halogenated neutral or electronegative group such as O, COOH, OH, OCH_3 OC_2H_5, CH_3 and C_2H_5 among others but at least one of R_{2-6} must be a low molecular weight group. Examples of such compounds include the naturally occurring sinapic, caffeic, coumaric, chlorogenic and ferulic acids as well as eugenol, and anethole among others. These compounds, impart pleasant or unique desirable and distinctive flavour to tea beverages when properly combined. These also contribute to the stability of the beverage and may be used alone or in combination with mild heat treatments or reduced levels of traditional chemical preservatives such as sorbic and/or benzoic acid and their salts. They also contribute to antimicrobial activity at both ambient and chilled temperatures.

As mentioned above acidified and native pH based tea beverages including juice flavoured and juice containing tea beverages in the 2.5-7.0 pH range are known to be susceptible to spoilage by yeast, mould, acid tolerant bacteria (e.g. *Lactobacillus sp, Gluconobacter/Acetobacter sp.)* and/or mesophilic or thermophilic spore forming (e.g. *B. coagulans* and the *Alicyclobacillus sp.)* and non-spore forming bacteria. The compounds of the invention such as 3,4-dihydroxycinnamic acids (i.e. caffeic acid), 4-hydroxy-3-methoxycinnamic acid (i.e. ferulic acid) and 3-caffeoylquinic acid (i.e.chlorogenic acid) alone, when formulated in combination with low levels of sorbic or benzoic acid and mixtures of these as well as other flavour components contribute to a pleasant unique, desirable and distinctive flavoured tea while adding the benefit of their antimicrobial activity. The compounds may be used at individual concentrations of preferably from about 25 to about 600 ppm and while used primarily as a flavourant have been found to be extremely effective antimicrobials. The compounds are effective against yeast, mould, and other acid tolerant and non-acid tolerant spore-forming and non-spore-forming spoilage bacteria in ready-to-drink tea beverages and tea beverages containing juice, fruit or vegetable extracts and/or additional flavours.

Higher levels of the compounds of the invention up to about 2,000 ppm or higher may be used if desired.

The increased efficacy of these compounds as antimicrobials, relative to a simple phenolic acid like benzoic acid, is believed to be attributable to the presence of an unsaturated side chain. The efficacy of this side chain

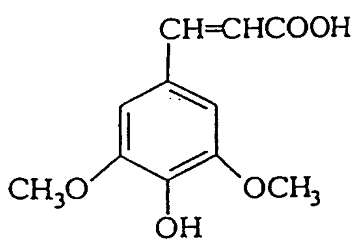
increases with the length of the side chain and the number of reactive double bonds contained in the same. The presence of these double bonds enhances the reactivity of the compound, internal to the microbial cell, after passive transport of the compound into the cell. This is similar to the transport of benzoic acid into the cell. The subsequent combination effects of the dissociation of the acid moiety internal to the cell, and the accompanying presence of one or more highly reactive double bonds, contributes significantly to the antimicrobial effect observed. Small chemical groups that release, or by virtue of their bonding structure, readily share electrons significantly stabilise the benzene ring's electrical charge and reduce the amount of energy needed to force reactions to take place at other sites on the ring. Relatively small electron withdrawing groups at other sites on the ring destabilise it and are therefore more easily released as highly reactive charged species or free radicals. The combination of these electron releasing and electron withdrawing species on the same ring provides unique reactive properties.

The small size of the attached groups facilitates passage through the cell membrane and concentrates the energy of reaction once inside the cell. These combinations include H, OH, CH_3, NH_2, OCH_3 as "activating" (electron releasing) groups, and COOH, $COCH_3$, CHO, NO_2 alone or attached to short unsaturated carbon chains, as electron withdrawing groups that become released as highly reactive charged or free radical species.

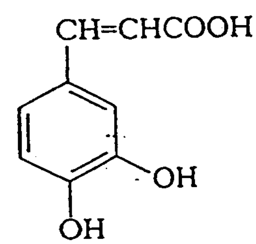
The use of the disclosed class of compounds, both naturally derived and synthetically prepared, provides a portfolio of

antimicrobial compounds that may be used to formulate beverages which are "all-natural", by the current definition of the term. Pleasantly flavoured, ready-to-drink still and carbonated tea beverages that are stable and safe at ambient temperatures and/or that have an extended shelf life at chill temperatures are thus enabled. Further, the flexibility of the class of compounds affords a broad selection of agents suited to complement enhance and/or contribute of unique, desirable and distinctive flavour to the flavour profile of the tea beverage system

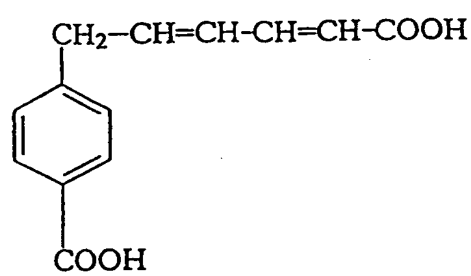
Some specific examples of the compounds are as follows:



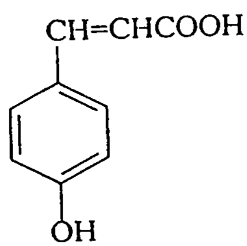
Sinapic Acid



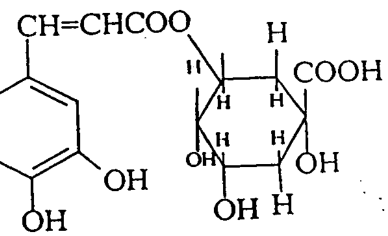
Caffeic Acid



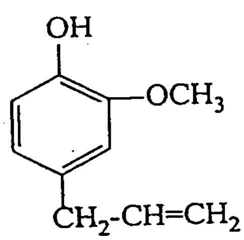
4-Carboxybenzylsorbic Acid



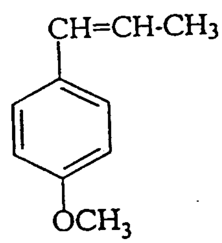
p-Coumaric Acid



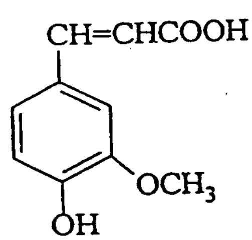
Chlorogenic Acid



Eugenol



Anethole



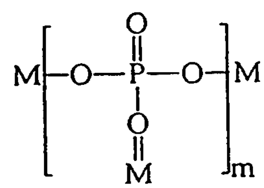
Ferulic Acid

While not wishing to be bound thereby, it is theorized that the antimicrobial material operates as follows: Essentially the organism will typically passively transport the compound class described, in its non-dissociated (unchanged) state. Once the compound is in the cell it begins to dissociate, essentially upsetting the pH balance internal to the cell. An organism such as *Z. bailii*, one of the yeast species that poses a serious spoilage problem in beverages is reported to possess an ability to pump a preservative such as benzoic acid out quite readily thus, leading to *Z. baiiii's* reputation as being somewhat preservative resistant. The compounds of the present invention are less likely to succumb to the preservative pump because of added high reactivity of the unsaturated side chain. It is believed that for this reason compounds of the type disclosed are effective.

In addition to the selected flagrant for tea beverages it is advantageous to lower the pH to about 2.5 to 4.0 to improve the beverage stability. This is particularly useful when fruit juices or fruit flavours are employed in ready to drink tea beverages such as lemon flavoured tea beverages.

Further it has been found that the flavourant/antimicrobial compounds of the invention provide improved stability in tea beverages when the magnesium and calcium ions common to tap water are kept to a minimum of no more than about 300 ppm as $CaCO_3$. Preferably the hardness is less than about 100 ppm and most preferably less than about 50 ppm or even lower such as 25 ppm or less. This can be achieved by deionization reverse osmosis or ion exchange in appropriate manner.

In addition it has been found that selected phosphates also contribute to stability and flavour and thus about 100 ppm to about 1000 ppm or higher and preferably about 250 to 500 ppm of a polyphosphate having the formula:



where m averages about 3 to 100 and M may be sodium or potassium.

Other preservatives such as sorbic acid or sorbate and benzoic acid or benzoates or parabens used alone or in combination at levels of about 50 to 1000 ppm provide a benefit without effecting flavour.

Additional sequestrants such as EDTA, NTA and the like have also been found to be useful in amounts of about 20 ppm up to about 1 000 ppm and preferably about 30 ppm to about 1000 ppm. When EDTA is used the lower levels are preferred.

Many suitable sequestrants are listed in the Handbook of Food Additives, 2nd Edition, edited by Furia, CRC Press,

As used herein, the term "tea concentrate" refers to a product derived from concentrated tea extract which is diluted with water to form a drinkable tea beverage. The method of extraction is not significant and any method known in the art may be used.

As used herein, the term "tea beverage" refers to a drinkable beverage prepared from tea concentrates, extracts or powder. Usually the beverage is prepared by mixing with water. Various other flavouring agents and/or juices may also be included in the tea beverage such as fruit juices, vegetable juices and the like. If a concentrate or powder is used then the concentrate or powder is generally diluted with sufficient water to provide the tea beverage. Preferred tea concentrates or powders are typically diluted to about 0.06 to 0.4% tea solids and preferably about 0.08 to 0.2% tea solids to provide a drinkable tea beverage but this depends on the flavour profile sought and amounts of 0.01 to 0.5% or higher may be used.

As used herein, the term "tea solids" refers to those solids normally present in a tea extract including normal tea antioxidants. Polyphenolic compounds are normally the primary component of tea solids when prepared from an extract of *Camellia sinensis*. However, tea solids can also include caffeine, proteins, amino acids, minerals and carbohydrates.

All parts and proportions herein and the appended claims are by weight unless otherwise indicated.

In order to demonstrate a stepwise or "hurdle" approach to achieving microbiological stability, several sets of experiments were run to establish the benefit of employing this approach. The individual steps are as follows:

1. water with a low water hardness;
2. pH control;
3. sequestrants including EDTA;
4. polyphosphate;
5. benzoate;
6. sorbate;
7. The compounds of the invention.

A ready to drink (RTD) tea composition containing about 0.08% tea solids was prepared having the following general composition.

K Sorbate	.04%
K Benzoate	.03%
Citric Acid	.07%
Tea Powder	.08%
Colour Component	.06%
Lemon Flavour	. 1%
HFCS (High Fructose Corn Syrup 55DE)	12%
Water balance to	100%

pH adjusted to 2.8 with phosphoric acid.

EXAMPLE 1

Water hardness measured as $Ca(CO_3)$ in the presence and absence of 30 pp of EDTA was studied at different water hardness levels including 28 ppm; 36 ppm; 72 ppm and 138 ppm.

The RTD beverage was prepared as above at several water hardness levels and inoculated with *Z bailii*, preservative resistant spoilage yeast at a level of 10 colony forming units (CFU) per ml of beverage. The beverage was then bottled and observed for failure such as a plate count with at least a 2 log increase; or "Frank Spoilage" such as for example $C0_2$ production or sediment or the like. Tabular results follows:

TABLE 1

Cumulative percent of bottles that have failed										
28 ppm water hardness										
	with EDTA					without EDTA				
weeks	1	5	8	13	16	1	5	8	13	16
%	0	0	0	0	0	0	0	0	0	0

TABLE 2

Cumulative percent of bottles that have failed										
36 ppm water hardness										
	with EDTA					without EDTA				
weeks	1	5	8	13	16	1	5	8	13	16
%	0	0	0	0	3	0	0	0	0	5

TABLE 3

Cumulative percent of bottles that have failed										
72 ppm water hardness										
	with EDTA					without EDTA				
weeks	1	5	8	13	16	1	5	8	13	16
%	0	0	0	3	3	0	0	0	100	-

TABLE 4

Cumulative percent of bottles that have failed										
138 ppm water hardness										
	with EDTA					without EDTA				
weeks	1	5	8	13	16	1	5	8	13	16
%	0	11	73	83	87	0	100	-	-	-

These results clearly show that increasing water hardness reduces the microbial stability of the beverages and the addition of EDTA increases the microbial stability of the beverages. The addition of EDTA has been reported to destabilise the microbial cell wall and cell membrane. Accordingly, EDTA is theorized to have the effect of contributing to stability of the beverage by reducing water hardness, chelating metals and increasing the permeability of the microbial cell wall to preservatives by destabilising the wall and membrane.

EXAMPLE 2

A study was done to determine the impact of hexametaphosphate at a level of about 500 ppm at a pH of 2.8 and 3.2. An RTD beverage was prepared and bottled as in Example 1 except it contained 30 ppm EDTA and the water hardness was 50 ppm.

The beverage was inoculated with *Z bailii* at 1 CFU and 10 CFU. Hexametaphosphate was either present or absent.

TABLE 5

pH 2.8 - 1 CFU - Cumulative % Failures					
weeks	2	4	6	8	10
sodium hexametaphosphate 0 ppm	8	100	-	-	-
sodium hexametaphosphate 500 ppm	0	0	3	84	100

TABLE 6

pH 2.8 - 10 CFU - Cumulative % Failures					
weeks	2	4	6	8	10
sodium hexametapphosphate 0 ppm	47	100	-	-	-
sodium hexametaphosphate 500 ppm	0	0	100	-	-

TABLE 7

pH 3.2 - 1 CFU - Cumulative % Failures							
weeks	1	2	3	4	6	8	10
sodium hexametaphosphate 0 ppm	0	0	89	100	-	-	-
sodium hexametaphosphate 500 ppm	0	0	3	100	-	-	-

TABLE 8

pH 3.2 - 10 CFU - Cumulative % Failures							
weeks	1	2	3	4	6	8	10
sodium hexametaphosphate 0 ppm	0	39	100	-	-	-	-
sodium hexametaphosphate 500 ppm	0	0	100	-	-	-	-

The results clearly show the enhancement in the delay of the onset of spoilage by the use of hexametaphosphate. Additionally this reinforces that lower pH contributes to the microbial stability of the beverage.

EXAMPLE 3

A study examined the effect of pH at 2.8 and 3.1 in the presence and/or absence of benzoic and sorbic acids. The RTD beverage was prepared as in Example 1 except that 30 ppm of EDTA was added, the amount and presence of sorbic acid and benzoic acid was varied and the water hardness was set at 50 ppm. The inoculum used was 1 CFU/ml beverage of *Z baiiii* preservative resistant yeast:

Tabular results follow:

TABLE 9

Benzoic acid - 0 ppm Sorbic acid 200 ppm						
Cumulative % of Failures						
pH 3.1						
Weeks	2	4	6	8	10	12
%	0	11	43	54	54	62
pH 2.8						
%	0	0	0	0	3	3

TABLE 10

Benzoic acid - 200 ppm Sorbic acid 0 ppm						
Cumulative % of Failures						
pH 3.1						
Weeks	2	4	6	8	10	12
%	0	44	92	92	92	94
pH 2.8						
%	0	0	8	11	14	14

TABLE 11

Benzoic acid - 100 ppm Sorbic acid 100 ppm						
Cumulative % of Failures						
pH 3.1						
Weeks	2	4	6	8	10	12
%	0	3	8	14	14	14
pH 2.8						
%	0	0	0	0	0	0

These results demonstrate the synergistic effect of the combination of sorbic acid benzoic acid as well as the effect of lower pH on microbial stability of the beverage.

EXAMPLE 4

A study was run to screen for the effect of the compounds of the invention on microbial stability in a tea beverage.

The tea beverage was prepared from tea extracted with hot water and containing about 0.12% tea solids. The tea extract was sweetened with high fructose corn syrup and flavoured with lemon flavour and citric acid to form the beverage. The pH was 2.8. A sorbate/benzoate control (Control A) was prepared from the above beverage by adding 200 ppm benzoic acid and 300 ppm sorbic acid. An unpreserved control (control B), prepared from the same beverage but having no sorbate or benzoate was also included.

In addition to the controls four test formulations were prepared by adding to the above beverage test compounds as follows:

1.	ferulic acid	200 ppm
2.	coumaric acid	200 ppm
3.	sinapic acid	200 ppm
4.	caffeic acid	220 ppm

The tests were run in triplicate in 10 ml. culture tubes. Each tube was inoculated with 1 CFU/ml of beverage of Z *bailii* preservative resistant yeast. The results are reported as follows:

TABLE 12

Days to Obvious "Frank Spoilage" i.e. Gassing

weeks	1	2	3	4	5	6	7	8	9
Control A	0/3	0/3	0/3	0/3	0/3	0/3	1/3	1/3	2/9
Control B	0/3	0/3	0/3	0/3	0/3	3/3	3/3	3/3	3/3
Ferulic acid	0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	1/3
Coumaric acid	0/3	0/3	0/3	0/3	0/3	0/3	1/3	2/3	3/3
Sinapic acid	0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3
Caffeic acid	0/3	0/3	0/3	0/3	1/3	1/3	2/3	3/3	3/3

These results show that the compounds of the invention convey an antimicrobial effect in a tea beverage. The effect is comparable to and in a few cases better than the benzoic/sorbic acid combination.

The compounds could be ranked relative to the benzoic acid/sorbic acid system. For example coumaric acid began gassing the same day as the benzoic/sorbic system which would give a coefficient of 1. Ferulic acid would have a coefficient of about 1.3.

EXAMPLE 5

A study was run to more precisely define the inhibitory effects of one of the flavouring components from Example 4. This study contained a tea beverage model containing the following components.

	Approximate
Yeast nitrogen broth base medium	0.6
fructose	4.7%
glucose	3.9
citric acid	.7
K benzoate	.03
K sorbate	.04
40% phosphoric acid	.15
sodium hexametaphosphate	.05
water - Reverse Osmosis < 7	
ppm hardness - balance to	100%
pH to	2.8

The study was run on a Lab Systems Bioscreen C. The model, both preserved and unpreserved, was used as a control, and caffeic acid was added to establish an antimicrobial effect. The cells were inoculated with 1000 CFU/mi of *Z baiiii* and the samples were run in triplicate. The results are based on time to turbidity detection for each replicate and are tabulated as follows:

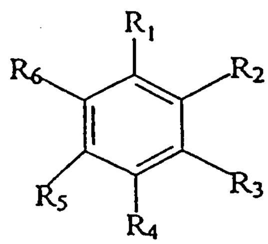
TABLE 13

Time to Turbidity Detection for Each Replicate	
Control Preserved	68-75-83 hours
Control unpreserved	19-19-20 hours
Caffeic acid 500 ppm	80-98-99 hours
Caffeic acid 1000 ppm	No turbidity detected in 3 replicates; 168 hrs
Caffeic acid 1500 ppm	No turbidity in 1 replicate; 79-89 hours
Caffeic acid 2000 ppm	82-88-97

This clearly shows improved microbiological stability by using caffeic acid.

CLAIMS:

1. A tea beverage containing a non-halogenated flavouring/antimicrobial compound of the formula:



wherein said R_1 is a moiety having up to nine carbon atoms and at least one double bond;

wherein said R_{2-6} groups may independently be H or a low molecular weight non-halogenated neutral or electron releasing group and at least one of said R_{2-6} groups is a low molecular weight non-halogenated neutral or electron releasing group, said compound being present in the beverage in an antimicrobial effective amount and said compound being capable of having a selective flavouring effect on said foodstuff.

2. An aqueous based beverage comprising at least about 0.02% to 0.5% tea solids by weight and a sufficient amount of the compound of claim 1 to prevent microbial spoilage.

3. A beverage as defined in claim 1 or 2 wherein said compound is present in an amount of at least about 20 to 2000 ppm.

4. A beverage as defined in any preceding claim having sufficient amount of said compound to completely inhibit the outgrowth of yeast, mould and other microbes.

5. A beverage as defined in any preceding claim further comprising sufficient tea solids to result in a significant antioxidant effect.

6. A beverage as defined in any preceding claim further comprising a flavouring agent and/or fruit or vegetable juice or extract in addition to tea.

7. A beverage as defined in claim 1 having a pH of 2.5 to 4.5.

8. A beverage as defined in claim 1 prepared from water having a total water hardness measured as $Ca(CO_3)$ of no greater than 50 ppm.

9. A beverage as defined in claim 1 having about 20 ppm to about 1000 ppm of a sequestrant other than citric acid.

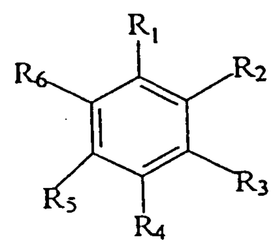
10. A beverage as defined in claim 1 having about 100 ppm to about 1,000 ppm of a polyphosphate.

11. A beverage as described in claim 1 having about 50 to 1000 ppm of a preservative selected from the group consisting of sorbic acid, sorbates, benzoic acid, benzoates, parabens and mixtures thereof.

12. A beverage as defined in claim 1 wherein said flavouring/antimicrobial compound is natural.

13. A beverage as defined in claim 1 wherein said flavouring/antimicrobial compound is synthetic.

14. A method for flavouring/preserving a tea beverage comprising adding to said beverage an antimicrobiologically effective amount of a compound of the formula



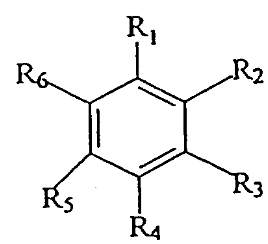
wherein said R_1 is a moiety having up to nine carbon atoms and at least one double bond;

wherein said R_{2-6} groups may independently be H or a low molecular weight non-halogenated neutral or electron releasing group and at least one of said R_{2-6} groups is a low molecular weight non-halogenated neutral or electron releasing group, said compound being present in the beverage in an antimicrobial effective amount and said compound being capable of having a selective flavouring effect on said foodstuff.

15. A method for improving the microbiological stability of a tea beverage comprising the steps of controlling the water hardness of said beverage to an incrementally antimicrobial level; controlling the pH of said beverage to an incrementally antimicrobial level; adding an incrementally antimicrobial effective amount of polyphosphate to said beverage; adding an incrementally

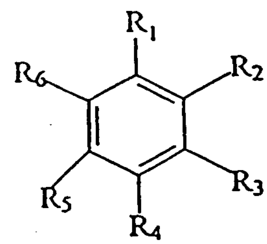
antimicrobial effective amount of a sequestrant other than polyphosphate to said beverage; adding an incrementally antimicrobial effective amount of benzoic acid or benzoate to said beverage;

adding an incrementally antimicrobial effective amount of sorbic acid or sorbate to said beverage; adding to said beverage an incrementally antimicrobial effective amount of a compound of the formula:



wherein said R_1 is a moiety having up to nine carbon atoms and at least one double bond; wherein said R_{2-6} groups may independently be H or a low molecular weight non-halogenated neutral or electron releasing group and at least one of said R_{2-6} groups is a low molecular weight non-halogenated neutral or electron releasing group and said compound being capable of having a selective flavouring effect on said foodstuff.

16. A tea beverage having a water hardness of about 25 ppm to 100 ppm measured a pH of less than about 3; about 200 to 700 ppm of sodium hexametaphosphate; about 10 to 75 ppm of EDTA; about 100 to 300 ppm of benzoic acid or benzoate; about 100 to 300 ppm of sorbic acid or sorbate; and about 10 to 1000 ppm of a compound of the formula:



wherein said R_1 is a moiety having up to nine carbon atoms and at least one double bond;

wherein said R_{2-6} groups may independently be H or a low molecular weight non-halogenated neutral or electron releasing group and at least one of said R_{2-6} groups is a low molecular weight non-halogenated neutral or electron releasing group, said compound being capable of having a selective flavouring effect on said foodstuff.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 98/06637

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A23F3/16 A23F3/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A23F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 016, no. 190 (C-0937), 8 May 1992 & JP 04 027374 A (T HASEGAWA CO LTD), 30 January 1992	1-5, 12-14
Y	see page 6 - page 11; claims 1-3	6-11
X	R. HORVAT: "A gas-liquid chromatographic method for analysis of phenolic acids in plants" JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY., vol. 28, 1980, pages 1292-1295, XP002093165 WASHINGTON US see table II	1,3-5

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 February 1999	22/03/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Desmedt, G

1

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 98/06637

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X Y	PATENT ABSTRACTS OF JAPAN vol. 11, no. 18, 17 January 1987 & JP 61 195646 A (ANAN KORYO SANGYO) see abstract ---	1-5,12, 14 6-11
X Y	US 5 336 513 A (J. RIEMER) 9 August 1994 see column 1, line 63 - line 68; examples 4,5 ---	1-5,13, 14 6-11
A	DATABASE WPI Section Ch, Week 9532 Derwent Publications Ltd., London, GB; Class B04, AN 95-241234 XP002093167 & CN 1 088 739 A (WANG S), 6 July 1994 see abstract ---	1-5
Y	WO 97 21359 A (THE PROCTER & GAMBLE CO) 19 June 1997 see page 6 - page 9; claim 1 ---	6-8,10
Y	WO 97 30597 A (THE PROCTER & GAMBLE CO) 28 August 1997 see examples 4,5 ---	6,7,11
Y	US 4 748 033 A (S. SYFFERT) 31 May 1988 see column 4 - column 9; claims 1-8 ---	6,7,9-11
Y	US 5 431 940 A (J. CALDERAS) 11 July 1995 cited in the application see column 11; claims 1-6 ---	7,8,10, 11
A	PATENT ABSTRACTS OF JAPAN vol. 095, no. 011, 26 December 1995 & JP 07 194356 A (SANEI GEN F F I INC), 1 August 1995 see abstract -----	1

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 98/06637

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5336513	A	09-08-1994	NONE		
WO 9721359	A	19-06-1997	US	5641532 A	24-06-1997
			AU	1335597 A	03-07-1997
			CA	2240046 A	19-06-1997
			EP	0866665 A	30-09-1998
WO 9730597	A	28-08-1997	AU	1972997 A	10-09-1997
			EP	0884953 A	23-12-1998
US 4748033	A	31-05-1988	CA	1316753 A	27-04-1993
US 5431940	A	11-07-1995	AU	1924295 A	11-09-1995
			CA	2183536 A	31-08-1995
			CN	1144459 A	05-03-1997
			EP	0746212 A	11-12-1996
			JP	9509327 T	22-09-1997
			WO	9522910 A	31-08-1995